Effect of iron on the wetting, sintering ability, and the physical and mechanical properties of boron carbide composites: A review

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ABSTRACT

Due to its favorable physical, mechanical and chemical properties, boron carbide (B_4C) is one of the most important ceramics used in various industries. After diamond and boron nitride with a cubical structure, this material is the third hardest substance known; and due to its low density, large cross-sectional surface area for neutron absorption, excellent chemical stability, and other desired properties, it is considered as a strategic material. The sintering of boron carbide ceramics is very difficult due to the existence of strong covalent bonds in pure boron carbide and its low self-diffusion, high resistance against grain boundary slipping, and low surface energy. For these reasons, many additives have been added to boron carbide, as sintering aids. These additives, in addition to facilitating the sintering of boron carbide, do not have an adverse effect on its properties, and they improve the characteristics of the resulting product. Iron is one of the additives that reduces the sintering temperature and improves the mechanical properties of boron carbide by producing a liquid phase and thus preventing the growth of B_4C particles. In this paper, the role of iron additive in the wetting, sintering ability, and the physical and mechanical properties of boron carbide composites has been investigated.

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Contents

1. Introduction

Boron carbide is a substance with excellent hardness, low density, large cross-sectional surface area for neutron absorption and high chemical stability. After diamond and cubical boron nitride, this material has been known as the third hardest substance [1–3]. Because of the unique properties mentioned, B_4C ceramics have found extensive uses in various industries, including mechanical applications (e.g., in nozzle throats of missiles, as covers and coatings, as abrasives in polishing equipment, as protective armor material, etc.), chemical applications (e.g., in boronization, preparation of borides, making chemical flasks for working with acids and alkalis, in producing solid fuels for missiles, etc.), nuclear applications (e.g., in protecting and controlling nuclear reactors, because of its great neutron absorption capability, etc.) and electrical applications (e.g., in thermocouples up to a temperature of 2200 °C) [4–6]. The limitation in the use of B_4C pertains to its high chemical stability, which is mostly due to the difficulty of sintering B_4C because of the strong covalent bonds that exist within its crystalline lattice. Because of its high melting point, the common method of fabricating boron carbide parts involves the use of hot pressing technique, which is very costly and requires advanced equipment. Thus, for fabricating the B_4C parts, it is better, economically, to use the pressureless

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sintering of its powder form; which is less costly compared to the common methods. In order to obtain a compact product in a neural atmosphere or vacuum, pure and fine powders (<2 μm), high sintering temperatures (1373-1473 °C), pressure in the range of 30–40 MPa and a pressing time of 15–45 min in graphite molds are needed. For this reason, sintering aids are used for better sintering; which reduce the sintering temperature to about 2023–2173 °C. In forming the boron carbide powder, metallic sintering aids such as iron, aluminum, nickel, copper and other metals are used. Also, silicon carbide or carbon powders are utilized to control the grain sizes. On the subject of improving the sintering conditions of B_4C by adding various sintering aids, extensive research works have been carried out in the last several decades, and more investigations are still ongoing. According to the obtained results, some sintering aids help reduce the sintering temperature [7–9].

So far, the effects of many additives such as TiO_2 [10,11], TiB_2 [12,13], Y_2O_3 [5], Al_2O_3 [14], TiC [15], Si [16,17], Fe [18] and others on the sintering ability and properties of B_4C have been investigated. In this regards, the incentive of using iron is that it reacts with B_4C, free carbon is produced and, thus, the FeB phase is formed. The low melting point of FeB can facilitate the sintering conditions of the liquid phase as well [19]. The sintering of the liquid phase indicates the wetting of the solid by the carbon–boron–iron solution. In this paper, the effects of iron on the reduction of sintering temperature and thus the prevention of grain growth and the improvement of mechanical properties have been investigated. It has been attempted to present a complete report on the effects of iron additive on the wetting, sintering ability, and physical and mechanical properties of boron carbide composites.

2. Examining the wetting behavior in the B_4C–Fe system

A small number of investigations have been conducted on the wetting behavior in the B_4C–Fe system. Panasyuk et al. [20] have studied the wetting phenomenon in boron carbide systems containing aluminum, silicon, nickel and iron melts. In their research, they have measured the reaction angle and the speed of melt dispersion on the surface of B_4C. In the Fe melt, the initial contact angle of 60° reduces to 36° after 10 min; and after 25 min, the final angle becomes 35° (Fig. 1).

The slow speed of melt dispersion is due to the viscosity increase of the iron melt in the course of its reaction with B_4C and the formation of a new phase in the contact zone. The microstructure of the B_4C–Fe system indicates the existence of various phases including a metal matrix phase with a microhardness of 1200–1600 kgF/mm², eutectic region along grain boundaries, a boron carbide base region with a microhardness of 4000–6000 kgF/mm² and needle-shaped graphite deposits. The XRD
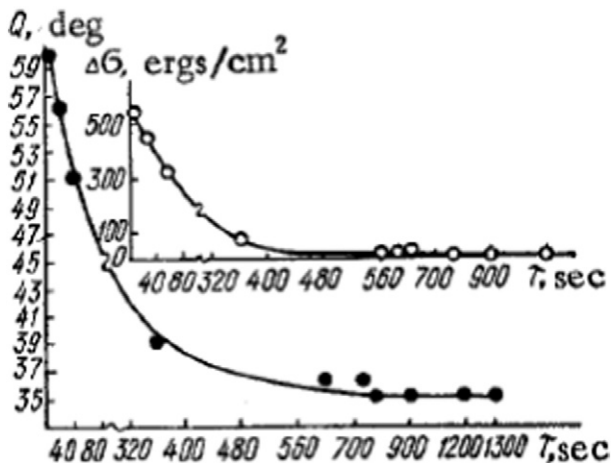
analysis indicates the presence of the FeB phase in the system. The contact between B_4C and melted iron causes a severe reaction between them, which decomposes boron carbide into B and C and eventually leads to the formation of FeB in the system. Also, the carbon component precipitates in the reaction zone, thereby increasing the viscosity and reducing the speed of melt dispersion. In this research, contact angles of 28, 20 and 46° have been measured for Al, Si and Ni, respectively [20].

To explore the effect of iron on the sintering ability and properties of B_4C, Aizenshtein et al. [21] have investigated the wetting of the B_4C/(Fe–C–B) system. Iron and its alloys along with carbon and boron react with the boron carbide sub-layer and form a region containing a mixture of FeB and graphite. The apparent contact angles for alloys with average concentrations of boron and carbon are relatively small and, consequently, the sintering of the liquid phase in the B_4C–Fe mixture is plausible. The sintering behavior and the densification process was investigated and monitored by a dilatometer. Dilatometric studies of sintering speeds confirm that the sintering of the liquid phase has really occurred and caused the improvement of material transfer. The macroscopic contact angles as a function of the amount of carbon or boron in the melt have been measured after 15 min of contact at temperature 1450 °C and presented in Table 1.

Table 1 indicates that, for the double melt of Fe–C, the wetting angle increases with the increase in the amount of carbon; while in the Fe–B melt, the wetting angle gradually diminishes with the increase in the quantity of B. Fig. 2 shows the SEM images of the reaction zone. The images taken from the cross sections of samples indicate that the reaction zones have formed at the sub-layer surface under the congealed droplets; therefore, the measured macroscopic contact angles should be considered as apparent contact angles. The depth of the reaction zone for iron-based alloys varies in the range of 15–45 μm and reaches 100 μm for pure Fe (Table 1 and Fig. 2).

In view of the EDS results, the reaction zone includes a mixture of FeB + C. Graphite precipitation occurs near the reaction zone, and its shape depends on the melt composition. The high degree of the decomposition of B_4C in contact with pure iron produces a large amount of carbon, which precipitates as rough graphite particles. These particles tend to be suspended within the melt and are situated above the reaction zone (Fig. 2(a)). When FeB comes into contact with the matrix, the amount of dissolved B_4C diminishes severely and needle-shaped graphite forms (Fig. 2(b)). Continuous graphite layers form when the Fe-rich alloy of B and C interact with the B_4C background matrix (Fig. 2(c)). Actually, the dissolving of a small amount of B_4C is sufficient for the saturation of metal melt with carbon and the precipitation of continuous graphite layers. In this case, the melt doesn't wet the matrix; and for the Fe–23B–6C alloy, a wetting angle of about 100° has been reported. The Dilatometric curves of density increase for B_4C and the mixture of B_4C–5.5 vol.% Fe have been illustrated in Fig. 3. The first instance of powder mixture compaction has occurred at 1473 °K. At a temperature of about 1750 °K, the powder sample containing Fe has severely contracted relative to the pure B_4C powder [19,21].

In order to investigate the speed of sintering and reactions that occur at the interfaces, the Isothermal sections of the Fe–B–C triple phase diagram have been shown in Fig. 4. These isothermal sections have been

Fig. 1. Changes of the reaction angle Q and the driving force of melt dispersion Δ ₆ versus time.

Table 1
Wetting angles and the depths of reaction zone for different compositions after 10 min of contact at 1450 °C.

Fe–B–C alloys (at.%)	Apparent content angle	Depth of the interaction zone (μm)
Fe	35° ± 3°	100° ± 8°
Fe–17B	30° ± 2°	25° ± 4°
Fe–32B	15° ± 3°	40° ± 5°
Fe–1.4C	36° ± 4°	47° ± 18°
Fe–10C	60° ± 3°	40° ± 3°
Fe–3B–3C	35° ± 3°	33° ± 6°
Fe–23B–6C	100° ± 5°	32° ± 4°
Fe–28B–3C	35° ± 3°	19° ± 4°